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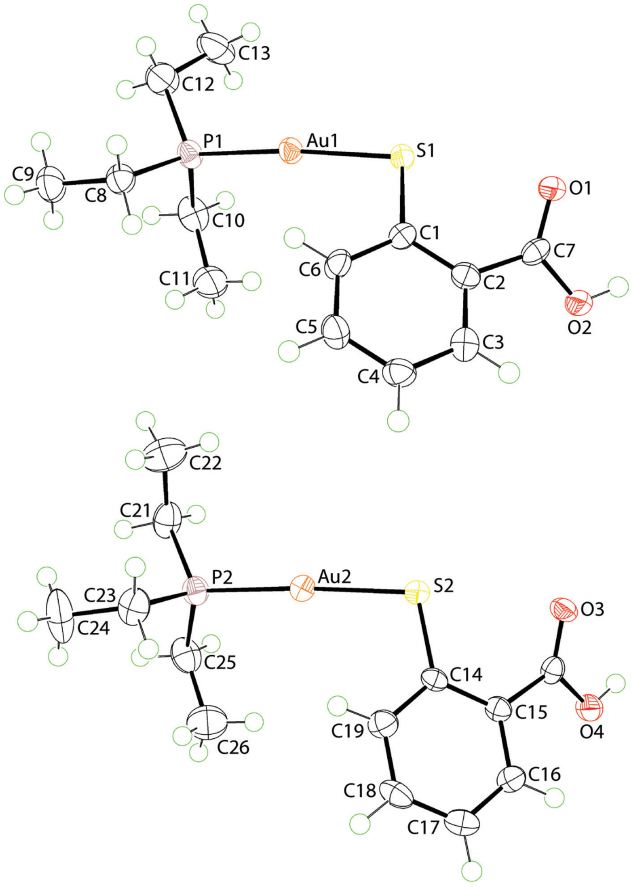
Crystal structure of [2-carboxybenzene-1-thiolato-*S*]-(triethylphosphane-*P*)-gold(I), $C_{13}H_{20}AuO_2PS$



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Abstract

$C_{13}H_{20}AuO_2PS$, triclinic, $P\bar{1}$ (no. 2), $a = 7.7509(2)$ Å, $b = 12.7840(3)$ Å, $c = 15.8689(4)$ Å, $\alpha = 89.087(2)°$, $\beta = 87.065(2)°$, $\gamma = 84.797(2)°$, $V = 1563.78(7)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0282$, $wR_{ref}(F^2) = 0.0795$, $T = 100$ K.

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The molecular structures are shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.12 × 0.12 × 0.10 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	19.8 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	33726, 5582, 0.026
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5541
$N(param)_{refined}$:	337
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

NaOH (Merck, 0.020 g, 0.5 mmol) in water (1 mL) was added to Et_3PAuCl (0.175 g, 0.5 mmol) in acetonitrile (15 mL), followed by the addition of 2-thiosalicylic acid (Merck, 0.077, 0.5 mmol) in chloroform (15 mL). The solution was stirred at room temperature for 2 h and left for slow evaporation, yielding yellow crystals after 3 weeks.

Yield: 0.192 g (82%). **M. pt.** (Biobase automatic melting point apparatus MP450): 378–379 K. Anal. Calc. for $C_{13}H_{20}AuO_2PS$: C, 33.34; H, 4.30. Found: C, 33.16; H, 4.45%. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{-1}): 2962 (w) ν(O–H), 1675 (s) ν(C=O), 1034 (s) ν(C–S). **^{1}H NMR** (Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane in $CDCl_3$ solution at 298 K, ppm): δ 13.38 (s, br, 1H, COOH), 8.31 (d, 1H, aryl-H1, $^3J_{HH} = 7.76$ Hz), 7.64 (d, 1H, aryl-H4, $^3J_{HH} = 7.75$ Hz), 7.28 (td, 1H, aryl-H3, $^3J_{HH} = 7.46$ Hz, $^4J_{HH} = 1.42$ Hz), 7.19 (t, 1H, aryl-H2, $^3J_{HH} = 7.55$ Hz), 1.83

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Au1	0.50883(3)	0.00400(2)	0.62533(2)	0.01695(8)
S1	0.51936(19)	0.15960(11)	0.54900(10)	0.0176(3)
P1	0.4835(2)	−0.13732(13)	0.71078(10)	0.0197(3)
O1	0.5054(6)	0.3766(3)	0.4836(3)	0.0243(10)
O2	0.2764(6)	0.4800(3)	0.5335(3)	0.0239(10)
H2O	0.342(9)	0.528(5)	0.523(5)	0.036*
C1	0.2995(8)	0.1966(5)	0.5296(4)	0.0163(12)
C2	0.2379(8)	0.3014(5)	0.5143(4)	0.0192(13)
C3	0.0597(9)	0.3287(5)	0.5028(4)	0.0211(13)
H3	0.019177	0.400267	0.494073	0.025*
C4	−0.0566(8)	0.2525(5)	0.5042(4)	0.0218(13)
H4	−0.175666	0.270843	0.494799	0.026*
C5	0.0035(9)	0.1494(5)	0.5194(4)	0.0233(14)
H5	−0.075813	0.096854	0.521893	0.028*
C6	0.1779(8)	0.1211(5)	0.5310(4)	0.0203(13)
H6	0.215939	0.049248	0.540148	0.024*
C7	0.3519(8)	0.3881(5)	0.5094(4)	0.0176(12)
C8	0.3280(9)	−0.2210(5)	0.6735(4)	0.0226(14)
H8A	0.215762	−0.178135	0.669032	0.027*
H8B	0.367329	−0.243977	0.615847	0.027*
C9	0.2958(10)	−0.3189(6)	0.7268(5)	0.0315(16)
H9A	0.406259	−0.360931	0.734169	0.047*
H9B	0.217131	−0.360728	0.698132	0.047*
H9C	0.243541	−0.297585	0.782097	0.047*
C10	0.4053(9)	−0.0953(6)	0.8157(4)	0.0267(15)
H10A	0.392158	−0.157890	0.852179	0.032*
H10B	0.492153	−0.054046	0.840284	0.032*
C11	0.2321(10)	−0.0287(6)	0.8148(5)	0.0351(17)
H11A	0.242097	0.030508	0.775329	0.053*
H11B	0.200238	−0.001986	0.871513	0.053*
H11C	0.142545	−0.071719	0.796789	0.053*
C12	0.6804(9)	−0.2244(6)	0.7250(5)	0.0321(16)
H12A	0.659261	−0.273834	0.772234	0.039*
H12B	0.708177	−0.266118	0.673247	0.039*
C13	0.8354(9)	−0.1638(7)	0.7434(5)	0.0376(18)
H13A	0.866651	−0.121771	0.693694	0.056*
H13B	0.934210	−0.213525	0.756902	0.056*
H13C	0.804665	−0.117359	0.791430	0.056*
Au2	0.59078(3)	0.51272(2)	0.87572(2)	0.01876(8)
S2	0.57186(19)	0.65473(12)	0.96535(10)	0.0193(3)
P2	0.6184(2)	0.38291(13)	0.77943(10)	0.0214(3)
O3	0.5334(5)	0.8749(3)	1.0236(3)	0.0194(9)
O4	0.7240(6)	0.9782(3)	0.9625(3)	0.0219(9)
H4O	0.638(7)	1.023(5)	0.968(5)	0.033*
C14	0.7837(8)	0.6944(5)	0.9649(4)	0.0158(12)
C15	0.8173(8)	0.7990(5)	0.9791(4)	0.0167(12)
C16	0.9883(8)	0.8263(5)	0.9809(4)	0.0197(13)
H16	1.008377	0.897408	0.989856	0.024*
C17	1.1285(8)	0.7518(5)	0.9700(4)	0.0229(14)
H17	1.243781	0.770500	0.973433	0.027*
C18	1.0966(8)	0.6488(5)	0.9539(4)	0.0232(14)
H18	1.191391	0.597038	0.944968	0.028*
C19	0.9291(8)	0.6208(5)	0.9507(4)	0.0209(13)
H19	0.911223	0.550106	0.938723	0.025*
C20	0.6769(8)	0.8850(5)	0.9908(4)	0.0171(12)
C21	0.4200(9)	0.3413(6)	0.7394(5)	0.0284(15)
H21A	0.355127	0.402647	0.713204	0.034*
H21B	0.450985	0.288662	0.694858	0.034*
C22	0.3016(11)	0.2940(7)	0.8070(5)	0.0404(19)
H22A	0.366264	0.235349	0.835339	0.061*
H22B	0.202021	0.268595	0.780535	0.061*
H22C	0.260457	0.347805	0.848480	0.061*
C23	0.7411(10)	0.2658(5)	0.8204(5)	0.0280(15)
H23A	0.851327	0.286981	0.840825	0.034*
H23B	0.674297	0.239266	0.869828	0.034*
C24	0.7841(13)	0.1755(6)	0.7588(6)	0.046(2)
H24A	0.676841	0.155295	0.736149	0.069*
H24B	0.841928	0.115312	0.788345	0.069*
H24C	0.861153	0.198047	0.712449	0.069*
C25	0.7360(10)	0.4232(6)	0.6843(4)	0.0290(15)
H25A	0.755135	0.362778	0.645725	0.035*
H25B	0.663476	0.479354	0.655688	0.035*
C26	0.9112(11)	0.4634(7)	0.7002(5)	0.0416(19)
H26A	0.893056	0.526444	0.735021	0.062*
H26B	0.969476	0.480615	0.646145	0.062*
H26C	0.983284	0.408926	0.729547	0.062*

(dq, 6H, PCH_2, $^3J_{HH} = 7.71$ Hz, $^2J_{PH} = 9.80$ Hz), 1.17 (dt, 9H, CH_3, $^3J_{HH} = 7.65$ Hz, $^3J_{PH} = 18.77$ Hz) ppm. **$^{31}P\{^1H\}$** NMR {$CDCl_3$}: 37.5 ppm.

Experimental details

The carbon-bound H-atoms were placed in calculated positions (C—H = 0.95–0.99 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2–1.5U_{eq}(C). The O-bound H atoms were refined with O—H = 0.84 ± 0.01 Å and with U_{iso}(H) = 1.5U_{eq}(O). Owing to poor agreement, five reflections, i.e. (3 2 1), (3 5 7), (3 6 5), (3 3 7) and (−4 −1 9), were omitted from the final cycles of refinement. The maximum and minimum electron density peaks of 2.10 and 1.18 eÅ^{-3}, respectively, were located 2.07 and 0.82 Å from the Au2 and H25B atoms, respectively.

Comment

The structural chemistry of the *n*-mercaptobenzoic acids ($HSC_6H_4CO_2H$-n; n-HmbaH) and anions derived from these has been reviewed recently, i.e. n = 2 [5] and n = 3 & 4 [6]. Prominent among these are phosphanegold(I) species owing, in part, to unpredictable crystallisation outcomes despite the universal adoption of a linear P—Au—S coordination geometry. For example [7, 8], for Cy_3PAu(2-mbaH), two conformational polymorphs were isolated, one with the anticipated eight-membered {···HOCO}$_2$ synthon arising from hydroxyl-O—H···O(carbonyl) hydrogen bonds occurring about a centre of inversion so the dimeric aggregate

has an open conformation; Cy is cyclohexyl. The other conformation had a more spherical shape as an intramolecular hydroxyl-O—H···S(thiolate) hydrogen bond formed instead [7, 8]. In another study of binuclear molecules (dppe)[Au(2-mbaH)]$_2$ [9], supramolecular chains mediated by $\{\cdots HOCO\}_2$ synthons were formed but, when co-crystallised dimethyl sulphoxide (DMSO), zero dimensional aggregates formed instead owing to the presence of hydroxyl-O—H···O(DMSO) hydrogen bonding; dppe is $Ph_2PCH_2CH_2PPh_2$. Different solvates of (o-tolyl)$_3$PAu(2-mbaH) exhibited solvent-dependent solid-state photoluminescence [10], a trait often observed for phosphanegold(I) thiolates [11]. Complimenting the above are long-standing evaluations of biological potential, especially for anti-cancer [12] /anti-bacterial [13] activity, again, as often observed for phosphanegold(I) thiolate analogues [14]. The present crystal structure determination of the title compound Et_3PAu(2-mbaH), (I), was investigated in continuation of studies in this area.

The crystallographic asymmetric unit of (I) comprises two independent molecules as shown in the figure (70% displacement ellipsoids). The molecules have very similar conformations in which the gold atom is linearly coordinated by thiolate-S [Au1—S1 = 2.3180(15) Å; Au2—S2 = 2.3137(15) Å] and phosphane-P [Au1—P1 = 2.2583(16) Å; Au2—P2 = 2.2622(16) Å] atoms; the P1—Au1—S1 angle = 173.90(6)° and P2—Au2—S2 = 175.11(6)°. The differences in the C—O bond lengths [C1—O1, O2 = 1.235(8) and 1.317(7) Å; C20—O3, O4 = 1.221(8) and 1.341(8) Å] confirm protonation at each of the O2 and O4 atoms. The 2-mbaH ligand is not aligned to sit directly over the P—Au—S axis, rather is twisted as seen in the Au1—S1—C1—C2 torsion angle of 155.4(5)° [Au2—S2—C14—C15 = 151.5(5)°]. Finally, the carboxylic acid residues are directed away from the rest of the molecule to facilitate hydrogen bonding interactions.

The most prominent intermolecular interactions in the crystal of (I) are hydroxyl-O—H···O(carbonyl) hydrogen bonds occurring about a centre of inversion, indicating each molecule self-associates to form a dimeric aggregate [O2—H2o···O1^{i}: H2o···O1^{i} = 1.77(7) Å, O2···O1^{i} = 2.607(6) Å with angle at H2o = 171(6)° and O4—H4o···O3^{ii}: H4o···O3^{ii} = 1.78(6) Å, O4···O3^{ii} = 2.616(6) Å with angle at H4o = 176(7)° for symmetry operations (i): $1-x$, $1-y$, $1-z$ and (ii): $1-x$, $2-y$, $2-z$]. Globally, the Au1-aggregates assemble into homo-molecular layers in the *ab*-plane with the goldphosphane residues projecting to either side of the plane. A similar situation pertains for the Au2-aggregates. The layers stack alternatively along the *c*-axis. Within the Au1-layers, methylene-C—H···O(carbonyl) interactions are apparent [C8—H8b···O1^{iii}: H8b···O1^{iii} = 2.44 Å, C8···O1^{iii} = 3.347(8) Å with angle at H8b = 152° for (iii): $1-x$, $-y$, $1-z$]. Within the Au2-layers, the connections between molecules are of the type phenyl-C—H···S(thiolate) [C17—H17···S2^{iv}: H17···S2^{iv} = 2.82 Å, C17···S2^{iv} = 3.544(6) Å with angle at H17 = 134° for (iv): $1+x$, y, z]. The only apparent directional contacts between layers are methylene-C—H···S(thiolate) interactions [C21—H21b···S1: H21b···S1 = 2.86 Å, C21···S1 = 3.844(8) Å with angle at H21b = 171°].

The Hirshfeld surfaces and two-dimensional fingerprint plots were calculated for overall (I) and for each of the independent molecules. This was accomplished with Crystal Explorer 17 [15] following standard protocols [16]. For (I), most of the surface contacts involve H with the greatest contribution coming from H···H contacts [53.3%]. The next most dominant contacts are H···C/C···H [16.8%], H···O/O···H [15.9%], with characteristic spikes ascribed to the O—H···O hydrogen bonding, and H···S/S···H [8.1%]. Very similar percentage contributions to the surface contacts are noted for each of the Au1- and Au2-containing molecules. In terms of differentiating between the Au1- and Au2-molecules, H···H contacts are more dominant for the Au1-molecule [53.6 versus 51.4%] while the H···C/C···H [16.3 versus 16.9%], H···O/O···H [14.9 versus 15.7%] and H···S/S···H [9.1 versus 9.5%] contacts are marginally decreased.

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